

## Modeling of the Mechanism of Influence of the Defect Structure in a Polycrystalline Scandium Oxide on the Properties of the Thermal and Electrical Effects in Vacuum

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In the process of studying the mechanisms of influence of structural defects on properties in scandium oxide, the thermal and electrical effects in the temperature range 25 – 1800 °C in a vacuum, in the structure was detected a gradual phase transition of the ordered cubic type C in a disordered type C<sup>1</sup> in the temperature range of 400 – 1000 °C. Phase transformation is accompanied by the difference of the conductivity type of the charge carriers. Anion conductivity of charges in the structure of scandium oxide exist there is to 400 °C, with the energy of conductivity charges 2.46 eV. In scandium oxide in the interval temperatures 400 – 1000 °C in case there is a mixture of two types of conductivity anion and electronic. In the interval of temperatures 1600 – 1800 °C in case there is a change of the chemical composition of the oxide on the content of oxygen. With the help of the mathematical model of calculation of the elements of the structure of the change in the size of the radii of oxygen and anionic vacancies, which coincides with the change of parameters of elementary cells in the transition of the structure of C in C<sup>1</sup>.

**Keywords:** Scandium Oxide, the Defects of Structure, Conductivity, Phase Transitions.

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### 1. INTRODUCTION

Scandium oxide on the structure and properties applies to oxides type Me<sub>2</sub>O<sub>3</sub>, has a high melting point, is a semiconductor of n-type. In a cubic structure of type C – contains 25% of the structures ordered anionic vacancies, which are the elements of the structure. Structural vacancies can be combined with impurity atoms, forming complexes defects caused by various impacts on the material. The accumulation of such defects change the structure and properties of semiconductor oxide materials. Conductivity of the oxide materials depending on structure, phase transformations and heating in different environments, when applying the electric field: ion, electron, proton and mixed [1-3]. Materials of Sc<sub>2</sub>O<sub>3</sub> represent practical interest, as materials with electrical conductivity, which can be used in various fields of technology: in the form of converters of energy as sources of energy, solid fuel, materials of radio electronics [4].

Information in the literature on structural transformations of scandium oxide, change the type of the conductivity at phase transformations us is not detected.

The aim of this work is the modeling of the mechanisms of the influence of the defects of the structure on the changes of physical properties of polycrystalline scandium oxide at thermal and electrical effects in the temperature range 25 – 1800 °C in a vacuum. These studies will determine the changes in the structure and the type of conductivity of the oxide scandium.

### 2. RESEARCH

#### 2.1 Materials and methods of research

Structural properties and conductivity of oxides of rare-earth elements are interrelated. Changes in the structure and the type of conductivity of the oxide scan-

dium can learn when heated to a high temperature in a vacuum, by the method of high-temperature x-ray by the UVD -2000 to the x-ray machine in a Cu K $\alpha$  radiation (the vacuum of 10<sup>-3</sup> – 10<sup>-4</sup> Pa).

The sample was heated with a speed of 10 °C/min with a shutter speed of at each fixed temperature up to an equilibrium state. For this purpose used dense samples of scandium oxide with the elementary cell:  $a = 0,9845 \pm 0.0001$  nm at the same time, in the high-temperature console to x-ray machine in the study of the structure of the samples, carried out measurement of electric resistance to change in the current when applying a voltage. For this purpose in the butt-ends of a rectangular sample drilled holes for tungsten electrodes. The error of measurement of electric resistance was 3%.

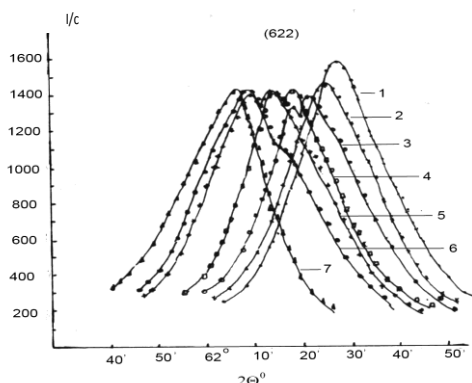
The parameter of a lattice determined with an error of  $\pm 0.0001$  nm. method of building a profile of x-ray lines of points in the interval of angles 10 – 70 ° in 2  $\theta$ . Then the applied voltage to the electrodes and the electric resistance was measure. The study sample was performed after every 100 °C.

#### 2.2 Mathematical model of phase transformation and the electrical conductivity in the structure of scandium oxide

When building a profile lines: (211), (222), (400), (622) it was found splitting them in the temperature range of 400 – 1000 °C, which corresponds to the phase transformation of the ordered phase type in a disordered type C<sup>1</sup>. The distance increased between the lines of the two phases in the range of 400 – 800 °C and above 800 °C gradually reducing the intensity of lines of the initial phase and convergence of them with the lines of a new phase. In the interval of 400 – 1000 °C there is a gradual transition

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in the disordered phase of the type  $C^1$  (Fig. 1).



**Fig. 1** – The profile of x-ray lines from the plane (622): 1 – 25 °C; 2 – 200 °C; 3 – 400 °C; 4 – 600 °C; 5 – 800 °C; 6 – 1000 °C; 7 – 1200 °C

This phase transition is the first kind and is reversible, if cool samples cool from the temperature is not above 1600 °C. Temperature 400 °C is the critical point for continuous functions  $y = f(C)$ :

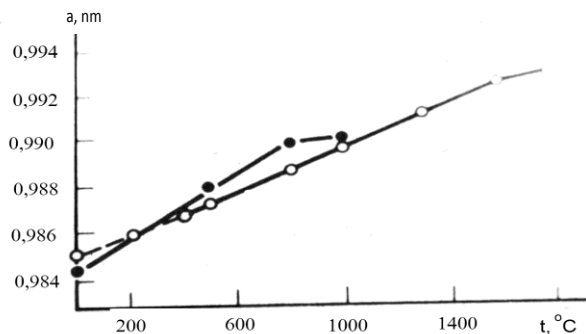
$$\lim_{t \rightarrow 400^\circ C} f(C) \quad \lim_{t \rightarrow 1000^\circ C} f(C + C^1) \rightarrow \lim_{t \rightarrow 1600^\circ} f(C^1) \quad (2.1)$$

This function suffers a break of the first kind and further moves in the disordered phase of the type  $C^1$ . A new phase is considered to be a disorderly in relation to the original. Similar transitions observed for oxide India [5].

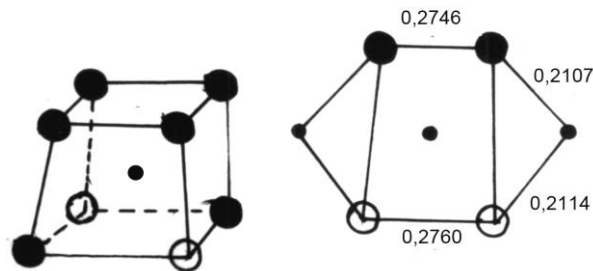
In Fig. 2 shows the dependence of the lattice parameter scandium oxide from the heating temperature. At 400 °C appear disorderly phase of scandium oxide. The volume of the elementary cell is on of the 0.002 nm<sup>3</sup> less than the ordered phase. Such a change of the volume of the elementary cell can be attributed to the reduction of the distortion of the crystal lattice by heating. If we extrapolate the value of the lattice of the disordered phase of the type of  $C^1$  up to room temperature, then define the parameter of a lattice, it is equal to  $a = 0.9852$  nm.

Let us consider the package of the atoms in the structure C type – ordered phase in the plane (110). She represents the distribution of atoms in the form of a wrong hexahedron.

Oxygen atoms and ordered anionic vacancy form is not the right cube, and the distorted prism, consisting of six oxygen atoms and two ordered anionic vacancies, which centered cations of scandium or free (Fig. 3).



**Fig. 2** – The depend of parameter of elementary cell of the scandium oxide from temperature



**Fig. 3** – Location of the atoms in the structure type C scandium oxide

Scandium oxide is a structural analogue of rare earth oxides, in the magnitude of the lattice parameter in the dependence on the radius of the cation falls in direct dependence on the scale of the Templeton and Doben according to data [5, 6], which confirms the belonging of the structure of the oxide of scandium at the rare earth oxides.

The parameter of a lattice ordered phase type C scandium oxide can be determined by means of ion radii as follows:

$$\frac{a}{2} = D_c \left( r_k + \frac{3}{4} r_a + \frac{1}{4} r_v \right) \quad (2.2)$$

where  $a$  – is a parameter of elementary cell;  $D_c$  – coefficient of cubic structures rarely land oxides on the scale of the Templeton and Doben ;  $r_k$  is the radius of the cation;  $r_a$  – ion radius of oxygen;  $r_v$  – ion radius of anionic vacancies.

For scandium oxide find values:  $r_k = 0.0734$  nm;  $r_a = 0.1373$  nm,  $r_v = 0.1380$  nm.

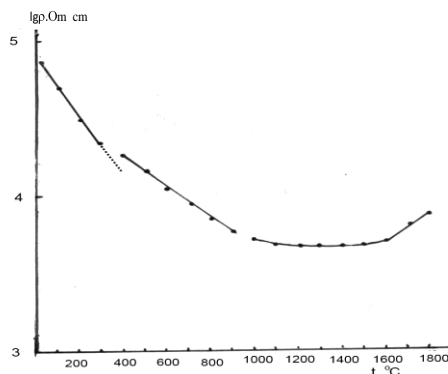
The difference of the lattice parameters of a disorderly and ordered phases obtained experimentally and the difference of ion radii anionic vacancies and of the oxygen atom, calculated by the equation (2) coincide and are 0.0007 nm.

The obtained values of the electrical resistance of the samples in the process of heating are shown in Fig. 4.

Experimental data indicate the existence of 4 plots direct, which have different inclinations, which points to 4 different mechanisms of conductivity. Such changes associated with different defects of the structure, which arise in the process of heating in vacuum.

In the temperature range 25 – 400 °C the ordered phase exists type C. The slope of the line in the temperature interval (Fig. 4) corresponds to the first type of conductivity. A structure of type C contains 25% of the anionic vacancies, which are the elements of the structure. The transition of these vacancies in the non-structural position in the heating leads to the reduction of distortions in the structure of ordered phases of type C, and the emergence of a disorderly type  $C^1$  phase. In the temperature range of 400 – 1000 °C there is a mixture of two phases C and  $C^1$ . In this temperature region the slope of a line changes, that points to the appearance of another mechanism of conductivity. In the structure appear plane, which does not contain anionic vacancies, in such planes appears electronic conductivity. Free electrons appear in the conduction band of the valence band of oxygen and 3d status

scandium. Mixed conductivity is a mixture of anionic vacancies and electrons.



**Fig. 4** – The temperature dependence of the electrical resistance of scandium oxide

In the interval of temperatures of 1000 – 1600 °C there is only electronic conductivity, which indicates on the constancy of electric resistance, and the presence on the x-ray graphs of one phase of the type C<sup>1</sup>. In the interval of temperatures 1600 – 1800 °C electrical resistance increases, which indicates the appearance of new structural anionic vacancies that arise as a result of evaporation of oxygen from the oxide. These vacancies are being implemented in the structural position and are sources of scattering of conduction electrons.

The energy of conductivity for each type of structures can be estimated by the equation of Boltzmann in various states of the system with relative probability, by analogy with the works [5-7].

The energy of anionic conductivity in the temperature range 25 – 400 °C is 2.46 eV, in the range of temperatures of 400 – 1000 °C in case there is a transition of anionic conductivity in the electronic conductivity. The phases C and C<sup>1</sup> are depends. The strength connection its phases is  $\rho = 0.47$ , where  $\rho$  – coefficient of regression. The energy is reduced by up to 1.58 eV and remains practically constant in the range 1000 – 1600 °C, which indicates the presence of only the disordered phase of the type C<sup>1</sup> with electronic conductivity.

Recovery of scandium oxide is above 1600 °C, which leads to growth of electric resistance and increase the energy of the conductivity of up to 2.19 eV.

The definition of carrier concentration and mobility in scandium oxide can be assessed on the value of the current density and the probability of conduction of charges in each interval of temperatures, in which changes the mechanism of conductivity.

For scandium oxide to change the density of the media free of charge in each interval of temperatures can be determined depending on their concentration:

$$n = j / e\sqrt{K/\rho} \quad (2.3)$$

where  $n$  – is the concentration of charge carriers,  $\sqrt{K/\rho} = \bar{v}$  – is the vector of average speed of ordered motion of charges in the environment:  $K$  – modulus of elasticity,  $\rho$  – density of the crystal by the data from [8];  $e$  – is the value of the charge carrier.

The probability of a drift of defects in ionic crystals is

determined according to [9]:

$$P = \nu \exp\left(-\frac{u_0 \pm ZeEd}{kT}\right) \quad (2.4)$$

where  $\nu$  – is the oscillation frequency of the atoms of the lattice;  $u_0$  – the initial difference of potential between the nodes of the lattice;  $Z_e$  is the charge of the carrier;  $d$  – the distance between the atoms of the lattice;  $E$  – electric field applied to the crystal.

Mobility of charge carriers for scandium oxide in the given experiment can be defined by the formula:

$$\mu \approx Zed^2 P / k(T_2 - T_1) \quad (2.5)$$

where  $k$  – is the Boltzmann constant.

When the ionic conductivity of the oxide of scandium (Fig. 4), in the areas of oxygen-anion vacancy, to calculate the mobility of media charges, take the distance  $d$  between the anion and anionic vacancies to increase this distance by the temperature in each interval of temperatures (Fig. 2). The probability of occurrence of different types of conductivity calculated based on the geometric probability, the method of relations areas of triangles (figure 4) in the temperature ranges of the 25 – 1800 °C, concentration and mobility of charge carriers in scandium oxide are shown in (Table 1).

Apparently, the increase in the concentration of free electrons and their mobility in the zone of the conductivity occurs by changing the structure of oxide, into which the plane, free from structural vacancies. In such planes electrons with ions of oxygen and cations scandium moving under the influence of electric field on the channels, in which there are no sources of scattering of electrons.

Structural vacancies shifting to non-structural position in which their influence on the scattering of electrons decreases. Such a change of the structure of scandium oxide occurs in a wide temperature range (673 – 1273 K), which leads to a phase transition C-C<sup>1</sup>.

In the structure of the disordered phase of the type C<sup>1</sup> concentration of charge carriers and their mobility is increasing due to the ionization of the atoms in the electric field.

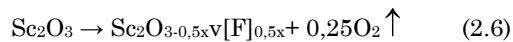
**Table 1** – Calculated values of the concentration of charge carriers their mobility, probability of various mechanisms of conductivity in scandium oxide.

T, K	300 – 673	673 – 1273	1273 – 1873	1873 – 2073
P – probability	0.16	0.25	0.40	0.19
$n$ , $10^{18} \text{ cm}^{-3}$	0.68	6.8	9.9	7.8
$\mu$ , $\text{cm}^2/\text{Vc}$	2.9	5.8	7.2	2.1

Such a structure is resistant to 1600 °C, above this temperature, the evaporation of the oxygen from the oxide and the appearance of new structural vacancies, which are the new sources of scattering of free charge carriers, which leads to local complex deformation interactions of the atoms in the lattice. In such areas the energy is absorbed, accompanied by the formation of local areas with broken-neutrality, which leads to growth of electric resistance, accompanied by a decrease slightly concentration of the carriers, and their

mobility is reduced significantly.

The emergence of additional structural anionic vacancies stabilizes the disordered phase of the type C<sup>1</sup>. Superfluous charge of the anionic vacancies is compensated by the formation of the centers of wet painting under the scheme:



where  $x$  – is the deviation from the norm of content oxide,  $v[\text{F}]$  – centers painting, which are formed by the reaction of:

$$\Delta\Phi = (\phi_{v(O)} / 2 - \phi_{v(F)} / 2 + A - 0,25F)x - \gamma k T \ln \Delta V / V \quad (2.8)$$

where  $\phi_{v(O)}$  – is the energy of education anionic vacancies,  $\phi_{v[F]}$  – energy education centre of the painting,  $A$  – the energy of affinity anion to the electron,  $F$  – the energy of transition of oxygen in the environment,  $\gamma$  – a factor that takes into account the change in volume of around defect, as the ratio of the radius of anionic vacancies to the radius of the oxygen-change,  $\Delta V$  – change of the volume of the elementary cell in the formation of additional anionic vacancies.

Such a mechanism of influence of the defects of structure explains the change: energy conductivity, wet painting samples, the elementary cell of scandium oxide in the interval of temperatures 1600 – 1800 °C in a vacuum.

### 3. SUMMARY

1. At the study of mechanisms of influence of structural defects on properties in scandium oxide at thermal and electrical effects in the temperature range 25 – 1600 °C in vacuum has been detected, the phase transition orderly type of the structure in the disordered type C<sup>1</sup>.

2. A mathematical model of calculation of the elements of the structure of scandium oxide, which allows you to determine the radii of the atoms on size of parameter of the unit cell. The calculated difference of the radii of anionic vacancies and oxygen coincides with the experimental value of the difference of the parameter of the lattice ordered type C and disorderly type C<sup>1</sup>.

3. Found that the phase transition is accompanied by various mechanisms of conductivity of ions in the temperature range 25 – 400 °C to electronic when the application is 1000 °C, in the temperature range of 1000 – 1600 °C in case there is only disordered phase type C<sup>1</sup> with electronic conductivity. In the interval of temperatures 1600 – 1800 °C in case there is a change of the chemical composition of the oxide and the appearance of new structural anionic vacancies, which lead to a change of the type of conductivity.

4. Mathematical model of recovery of scandium oxide helps to explain the stability of the disordered structure of type C<sup>1</sup> after cooling of the samples up to 25 °C.

5. Energy and the probability of different types of conductivity of the charge carriers were determine.

6. Modeling of the structural arrangements of atoms in the structure of scandium oxide in the heating and the imposition of an electric field with each type of conductivity, allowed calculate of the concentration and mobility of charge carriers to calculate and observe the changes, which are connected with the influence of defects.

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